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DOI: <https://doi.org/10.1007/s00706-008-0094-2>

Posted at the Zurich Open Repository and Archive, University of Zurich

ZORA URL: <https://doi.org/10.5167/uzh-13326>

Journal Article

Published Version

Originally published at:

Lopez-Hernandez, A; Venkatesan, K; Schmalle, H W; Berke, H (2009). Chemistry of chromium bis-acetylide complexes. *Monatshefte für Chemie / Chemical Monthly*, 140(7):845-857.

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Chemistry of chromium bis-acetylide complexes

A. López-Hernández · K. Venkatesan ·
H. W. Schmalle · Heinz Berke

Received: 14 August 2008 / Accepted: 21 October 2008 / Published online: 3 December 2008
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Abstract Stable paramagnetic Cr(II) and Cr(III) bis(alkynyl) complexes of the type $[trans(RC\equiv C)_2Cr(dmpe)_2]^{n+}$ ($R = Ph, SiMe_3, SiEt_3, C\equiv C-SiMe_3$ $n = 0, 1$) were prepared and characterised by NMR, cyclic voltammetry, EPR, magnetic measurements, and X-ray single-crystal diffraction studies.

Keywords Alkynes · Magnetic properties · Molecular wires · Oligomers · X-ray structure determination

Introduction

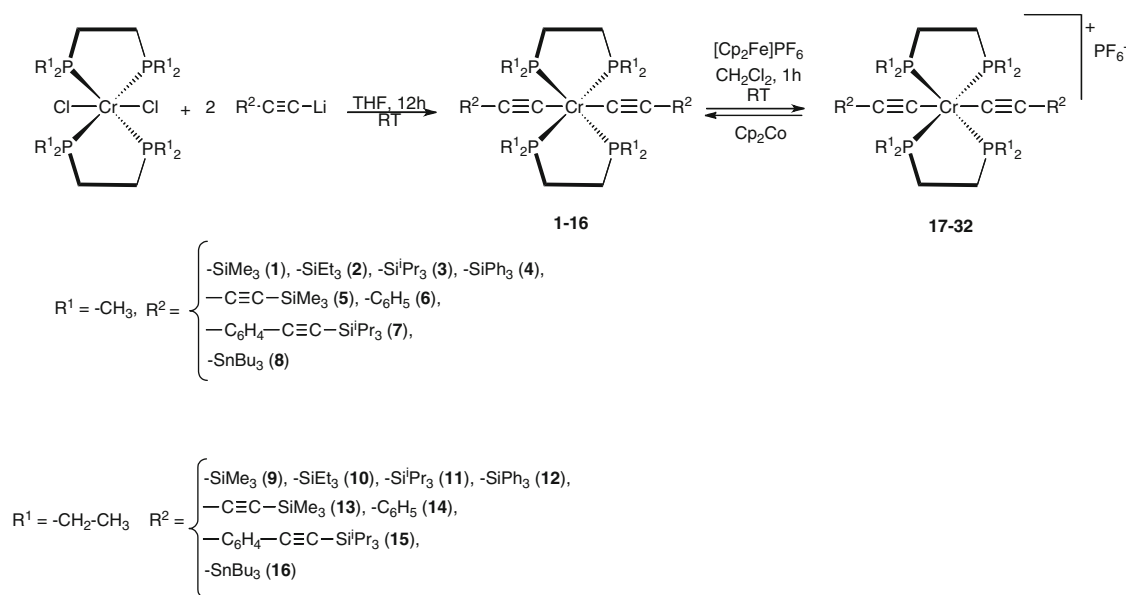
There is growing interest in complexes with *trans* σ -alkynyl ligands, because of their utilisation as building blocks in the synthesis of new dinuclear or oligonuclear rigid-rod complexes that can have potential applications as molecular wires [1–33]. Previous synthesis of similar bis-acetylide complexes has been limited to transition metals of groups VIII–X [25]. Paramagnetic analogues of such species have electronic open-shell configurations and are therefore expected to have nonlinear optical properties in addition to having applications as electronic materials in single-electron devices [1–3]. Strongly σ -donor ligand-substituted complexes of this type are expected to have low energy work functions, which is expected to guarantee strong electronic delocalisation and coupling between the metal centres [34, 35]. Only very recently a chromium bis-

acetylide complex has been reported [36]. Here we report the synthesis of redox-active mononuclear paramagnetic bis(alkynyl) chromium(II) and chromium(III) complexes and explore their electronic properties. We have previously shown that mononuclear complexes based on manganese centres bearing acetylide ligands can be coupled in a controlled fashion to yield dinuclear complexes [27–40]. Phosphine ligands as σ -donor ligands in these kinds of bisalkynyl complex have significant effects on the reactivity and redox properties of the complexes. For this reason both 1,2-bis(dimethylphosphino)ethane (dmpe) and 1,2-bis(diethylphosphino)ethane (depe) were utilised as the strongly binding ligands.

Results and discussion

Transition metals such as manganese bearing bis alkynyl compounds have previously been accessed by reaction of $Mn(dmpe)_2Br_2$ with the corresponding lithium acetylides [37–40]. Upon utilising similar reaction conditions, treatment of $CrCl_2(dmpe)_2$ and $CrCl_2(depe)_2$ [15] with two equivalents of $R-C\equiv C-Li$ ($R = -SiMe_3, -SiEt_3, -SiPr_3, -SiPh_3, -C\equiv C-SiMe_3, -C_6H_5-C_6H_5-C\equiv C-SiPr_3, -SnBu_3$) yielded the corresponding chromium(II)*trans*-bis(acetylide) complexes **1–16** quantitatively (Scheme 1). Extensive characterisation on these series of complexes with different silicon and tin end groups was accomplished. Strong paramagnetic behaviour of these complexes was observed by 1H NMR spectroscopy. The methylene and methyl proton resonances were found at high field between -3.1 and -34.0 ppm and broadening of the resonances in these complexes was caused by their paramagnetism. This was confirmed quantitatively by the temperature dependence of the chemical shifts following Curie–Weiss behaviour in the

A. López-Hernández · K. Venkatesan · H. W. Schmalle ·
H. Berke (✉)
Institute of Inorganic Chemistry, University of Zürich,
Winterthurerstrasse 190, 8057 Zürich, Switzerland
e-mail: hberke@aci.uzh.ch



Scheme 1

temperature range from -80 to 30 °C. In the Raman spectrum, the characteristic bands for the $(\text{C}\equiv\text{C})$ vibration and for the $(\text{C}-\text{H})$ vibrations of the methyl and methylene groups of the dmpe ligands were observed at around $2,000\text{ cm}^{-1}$ and between $2,900$ and $3,000\text{ cm}^{-1}$. The IR spectrum revealed similar bands for the $(\text{C}\equiv\text{C})$ vibration and for the $(\text{C}-\text{H})$ vibrations. This presumably is because of weak or even no coupling of the vibrations in the acetylenic groups.

Cyclic voltammetric studies performed on compound **1** showed a reversible one-electron oxidation step at -0.260 V ($\Delta E_p = 95\text{ mV}$) corresponding to the $\text{Cr(II)}/\text{Cr(III)}$ redox couple. Complexes **1–16** could be easily oxidised by use of ferrocenium hexafluorophosphate to afford the corresponding chromium(III) *trans*-bis(acetylide) complexes. The ^1H NMR spectra of the chromium(III) bis-acetylide complexes revealed very broad signals at highfield and lowfield between -30.2 and 41.0 ppm for the methylene and methyl protons of the dmpe and depe ligands. A significant shift from high field to low field was observed. In the ^{19}F NMR and ^{31}P NMR spectra a doublet and a septet, respectively, appeared corresponding to the PF_6^- counter anion. These signals were independent of the paramagnetic character of the complex confirming the non-coordinating nature of the PF_6^- anion. The Raman and IR spectra of the chromium(III) bis-acetylide complexes showed significant shifts for the $(\text{C}\equiv\text{C})$ vibration and for the $(\text{C}-\text{H})$ vibrations in comparison with the analogous chromium(II) bis-acetylide complexes.

The structure of complex **17** was confirmed by an X-ray diffraction study (Fig. 1). Yellow crystals were obtained from a dichloromethane solution at -30 °C. The

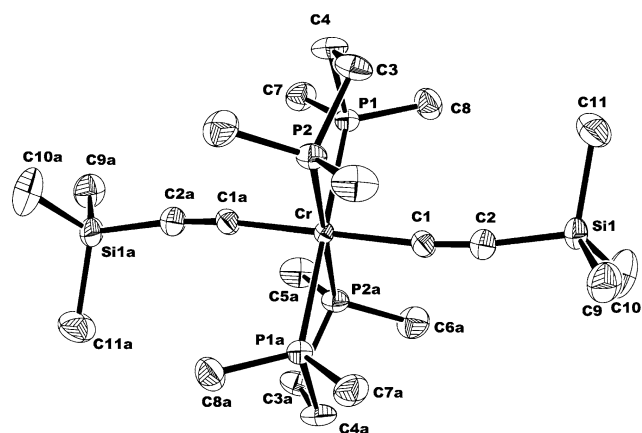


Fig. 1 X-ray structure of **17**. The ellipsoids are 50% probability and the hydrogen atoms, the counter anion PF_6^- , and solvent molecules are omitted for clarity. Selected bond lengths/Å and angles/°: $\text{Cr1}-\text{C1}$ $2.047(2)$, $\text{C1}-\text{C2}$ $1.200(3)$, $\text{C2}-\text{Si1}$ $1.833(2)$; $\text{C1}-\text{Cr1}-\text{P1}$ $90.46(6)$, $\text{Cr1}-\text{C1}-\text{C2}$ $174.24(18)$

compound crystallized in the monoclinic system. The $\text{Cr1}-\text{C1}$, $\text{C1}-\text{C2}$ and $\text{C2}-\text{Si1}$ bond distances are $2.047(2)\text{ Å}$, $1.200(3)\text{ Å}$ and $1.833(2)\text{ Å}$. The observed $\text{C1}-\text{Cr1}-\text{P1}$ and $\text{Cr1}-\text{C1}-\text{C2}$ bond angles were $90.46(6)^\circ$ and $174.24(18)^\circ$. In this molecule the chromium centre possesses octahedral coordination with the alkynyl ligands in a *trans* position and the P atoms in an equatorial arrangement displaying $\text{Cr}-\text{P}$ distances of $2.4459(5)$ and $2.4302(5)\text{ Å}$.

Single crystals of **22** were obtained by diffusion of ether into a saturated solution in CH_2Cl_2 at -30 °C. The structure of **22** was confirmed by X-ray diffraction analysis (Fig. 2). It crystallizes in the orthorhombic system in the Pccn space group. The $\text{Cr1}-\text{C7}$ and $\text{C7}-\text{C8}$ bond distances

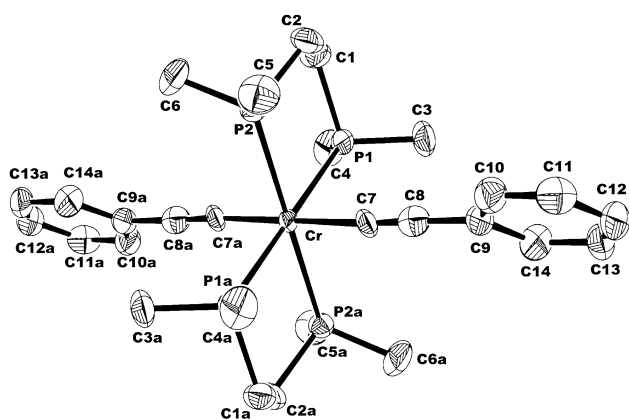


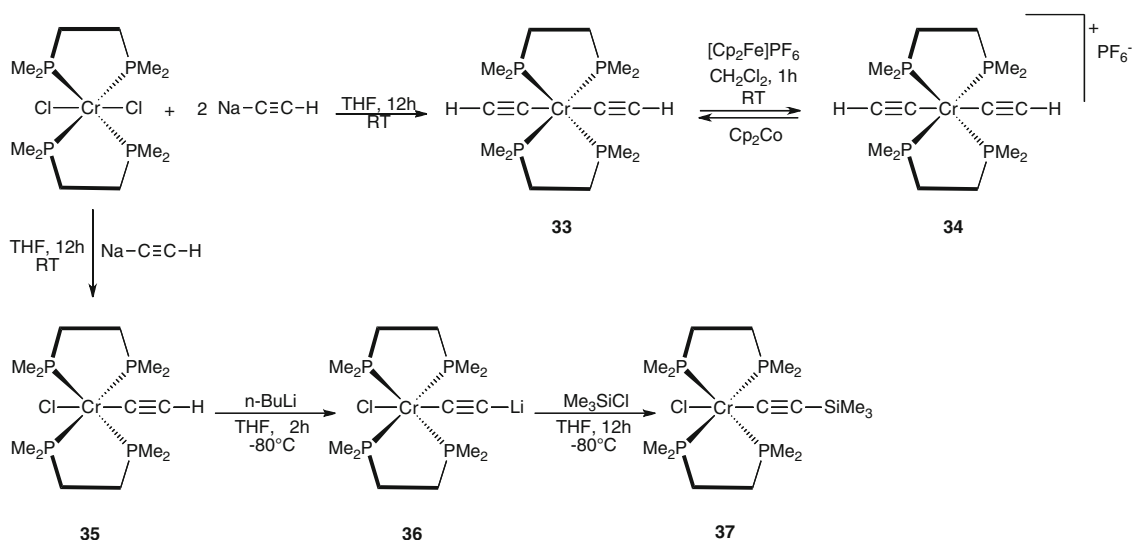
Fig. 2 X-ray structure of **22**. The ellipsoids are 50% probability and the hydrogen atoms and the counter anion PF_6^- are omitted for clarity. Selected bond lengths/Å and angles/°: Cr1–C7 2.095(2), C7–C8 1.120(3); C7–Cr1–P1 90.54(6), Cr1–C7–C8 173.8(2)

are 2.095(2) and 1.120(3) Å. The observed bond angles for C7–Cr1–P1 and Cr1–C7–C8 were 90.54(6) and 173.8(2)°, the unsaturated chain deviates slightly from linearity.

Direct synthesis of $[\text{trans-bis}\{1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}\}\text{-bis}(\text{ethynyl})\text{chromium(II)}]$, $\text{Cr}(\text{dmpe})_2(\text{C}\equiv\text{C-H})_2$ (**33**) was achieved by treating $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ with 2 equiv. sodium acetylide (Scheme 2). Controlling the reactivity of the terminal ends of these complexes is indeed very necessary to avoid polymer formation in subsequent reaction steps. Hence it is imperative to have different substituents on either side of the metal centre to react these molecules further in a controlled fashion. The reaction of $\text{CrCl}_2(\text{dmpe})_2$ with only 1 equiv. $\text{Na-C}\equiv\text{C-H}$ in tetrahydrofuran produced the corresponding mono-acetylide chromium complex $[\text{trans-bis}\{1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}\}(\text{chloro})(\text{ethynyl})\text{chromium(II)}]$ (**35**) in 62%

yield. The ^1H NMR spectra of complexes **33** and **35** revealed characteristic paramagnetic signals assignable to the protons of the methylene and the methyl protons of the dmpe ligands. The ^1H NMR resonances of the bis-acetylide mononuclear complex **35** of chromium appeared at high field as broad shifted signals at around -13.2 and -33.9 ppm for the methylene and methyl protons. Measurements of the temperature-dependent magnetic susceptibility were carried out for complexes **3** and **35**. A plot of the reciprocal susceptibility $1/\chi$ versus the temperature revealed Curie Weiss behaviour confirming paramagnetism, as had already been observed in the NMR measurements. Chromium(II) complex **3** had magnetic moments between $1.78 \mu_B$ and $2.21 \mu_B$ in the temperature range from 6 to 200 K. The magnetic moment of the chromium(II) complex indicated a low-spin d^4 configuration. Complex **35** has a magnetic moment between $2.96 \mu_B$ and $3.57 \mu_B$ in the temperature range from 6 to 200 K, values similar to those observed for the chromium(III) complexes, which are in agreement with the d^3 configuration (Fig. 3). An EPR spectrum of complex **35** recorded in frozen CH_2Cl_2 at 50 K shows a quintet which can be interpreted as the contribution from three unpaired electrons at $H = 3,372$ G ($g = 2.0023$) (Fig. 4). Super-hyperfine coupling constants of 38.2 and 4.6 G lead to the conclusion that these electrons are coupled to four chemically equivalent phosphorus nuclei and there is an additional field created by the hydrogen nucleus. The chromium(II) complexes showed EPR-silent behaviour under the same conditions in the temperature range from 50 to 300 K.

The structure of $\text{CrCl}(\text{dmpe})_2(\text{C}\equiv\text{C-H})$ **35** was established by X-ray diffraction studies (Fig. 5). The acetylide and chloro ligands are statistically disordered over two



Scheme 2

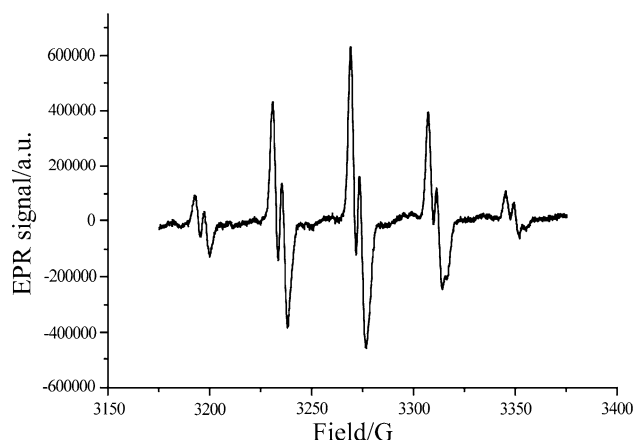


Fig. 3 EPR spectrum of complex **35** at 50 K in frozen glass

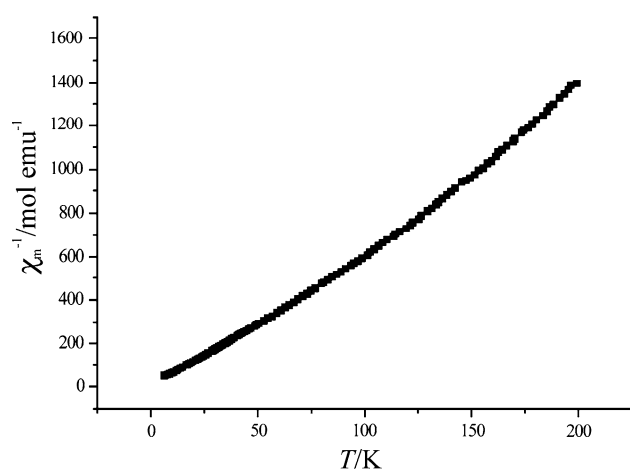


Fig. 4 Curie Weiss behaviour of **35**

sites with site occupation of 1/2, because the chromium atom lies on a crystallographic centre of inversion at (1/2, 0, 0). A structure solution in the non-centrosymmetric space group $P2_1$ showed the same acetylide chloro disorder with two $\text{C}\equiv\text{C}-\text{H}$ and two Cl atoms at each site. The compound crystallizes in the monoclinic system in the $P2_1/c$ space group. The Cr1–C7 and C7–C8 bond distances are 1.951(11) and 1.335(11) Å, respectively. The observed bond angles for C7–Cr1–P1 and P1–Cr1–P2 were 90.3(9) and 82.64(3)°.

Compound **35** was further reacted with 1 equiv. *n*-BuLi at -80°C and upon further treatment with Me_3SiCl , the unsymmetrically substituted complex **37** was isolated in 77% yield. The ^1H NMR spectrum of **37** revealed a broad singlet at 9.1 ppm for the methyl groups of the trimethylsilyl substituent. The corresponding methyl and methylene protons of the dmpe ligand appeared slightly high field shifted to -34.0 and -13.2 ppm. Compounds **35** and **37** offer many interesting reaction avenues that can potentially lead to dinuclear and oligonuclear complexes, which are currently being explored.

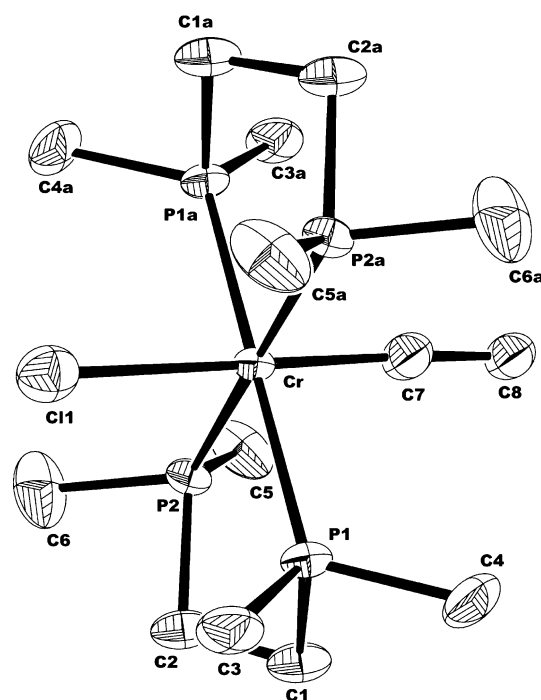


Fig. 5 X-ray structure of **35**. The ellipsoids are 50% probability and the hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths/Å and angles/°: Cr1–C7 1.951(11), C7–C8 1.335(11); C7–Cr1–P1 90.3(9), P1–Cr1–P2 82.64(3)

Conclusion

Chromium bis-acetylide complexes were obtained in good yields starting from $\text{CrCl}_2(\text{dmpe})_2$ and $\text{CrCl}_2(\text{depe})_2$. The corresponding chromium(III) complexes were produced in high yields of over 90% after oxidation of the chromium(II) complexes with ferrocenium hexafluorophosphate. Various bis-acetylide complexes were synthesised with different endgroups bearing silicon and tin substituents. All these complexes exhibit characteristic paramagnetic behaviour. These compounds have interesting electrochemical and magnetic properties. Tuning reaction conditions with sodium acetylide has led to the isolation and characterisation of the unsymmetrically substituted Cr(II) compound. The synthesised chromium acetylide complexes can serve as a very interesting and valuable starting material for the construction of dinuclear or oligonuclear compounds.

Experimental

All operations were carried out under an inert atmosphere of N_2 using Schlenk and vacuum-line techniques or in a glove box, model MB-150 B-G. The following solvents were dried and purified by distillation under nitrogen before use, employing appropriate drying/deoxygenating agents:

tetrahydrofuran (Na/benzophenone), toluene (sodium), CH_2Cl_2 (P_2O_5 , with filtration through active Alox). IR spectra were obtained on a Bio-Rad FTS instrument. Raman spectra were recorded on a Renishaw Ramanscope spectrometer (514 nm). EPR measurements were made on MPMS-5 S and PPMS-6000 instruments. ^1H NMR spectra were recorded on Unity 300 or Varian Gemini 200 spectrometers at 300 or 200 MHz. ^1H NMR Chemical shifts are reported in ppm units with respect to the signals of residual protons in the solvents and referenced to TMS. C and H elemental analysis was performed with a LECO CHN-932 microanalyzer; the results agreed favourably with the calculated values.

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(dichlorochromium(II), [Cr(dmpe)₂Cl₂] [15]

To a suspension of 100 mg CrCl_2 (0.81 mmol) in 15 cm^3 toluene was added 245 mg dmpe (1.62 mmol). The solution rapidly developed a brilliant apple green colour, and became noticeably warm. After 2 h, the solution was filtered, and the solvent was removed in vacuo. Crystallization from toluene produced large emerald green crystals. Yield: 277 mg (81%); ^1H NMR (toluene- d_8 , 300 MHz, 22 °C): δ = −13.3 (br, 8H, PCH_2), −34.0 (br, 24H, PCH_3) ppm; IR (ATR): $\bar{\nu}$ = 2,967 (w), 2,899 (w) (C–H), 926 (s), 888 (s) (P–C), 700 (m) (Cr–Cl) cm^{-1} ; Raman (514 nm): $\bar{\nu}$ = 2,966, 2,900 (C–H), 947 (Cr–P), 643 (Cr–Cl) cm^{-1} .

trans-Bis[1,2-bis(diethylphosphino)ethane]bis(dichlorochromium(II), [Cr(depe)₂Cl₂] [15]

To a suspension of 100 mg CrCl_2 (0.81 mmol) in 15 cm^3 toluene was added 334 mg depe (1.62 mmol). The solution rapidly developed a brown colour, and became noticeably warm. After 1 h, the solution was filtered, and the solvent was removed in vacuo. Crystallization from toluene produced large orange–green crystals. Yield: 385 mg (89%); ^1H NMR (toluene- d_8 , 300 MHz, 22 °C): δ = 3.7 (br, 24H, PCH_2CH_3), −15.4 (br, 40H, PCH_2CH_3), −23.8 (br, 8H, PCH_2) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,934 (w), 2,901 (w), 2,873 (w) (C–H), 1,030 (m), 983 (m) (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(trimethylsilylethynyl)chromium(II), [Cr(dmpe)₂(C \equiv C–SiMe₃)₂] (1, C₂₂H₅₀CrP₄Si₂)

A solution of 99 mg freshly prepared $\text{Li–C}\equiv\text{C–SiMe}_3$ (0.95 mmol) in 5 cm^3 THF was added to a THF solution of 200 mg $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ (0.47 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **1** was extracted with *n*-pentane. Crystallization from *n*-pentane produced large red crystals. Yield: 227 mg (88%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 8.9 (s, 18H, $\text{Si}(\text{CH}_3)_3$), −3.6 (br, 8H, PCH_2), −27.7 (br, 24H, PCH_3) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,975 (w), 2,898 (w) (C–H),

1,956 (m) (C \equiv C), 934 (s), 829 (s) (P–C) cm^{-1} ; Raman (514 nm): $\bar{\nu}$ = 2,961, 2,900 (C–H), 1,975 (C \equiv C), 698, 640 (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(triethylsilylethynyl)chromium(II), [Cr(dmpe)₂(C \equiv C–SiEt₃)₂] (2, C₂₈H₆₂CrP₄Si₂)

A THF solution (5 cm^3) of 138 mg freshly prepared $\text{Li–C}\equiv\text{C–SiEt}_3$ (0.95 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ (0.47 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **2** was extracted with *n*-pentane. Crystallization from *n*-pentane produced large red crystals. Yield: 298 mg (97%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 2.56 (s, 30 H, $\text{Si}(\text{CH}_2\text{CH}_3)_3$), −3.2 (br, 8H, PCH_2), −27.4 (br, 24H, PCH_3) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,949 (w), 2,903 (w) (C–H), 1,954 (m) (C \equiv C), 934 (s), 925 (s) (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(triisopropylsilylethynyl)chromium(II), [Cr(dmpe)₂(C \equiv C–Si i -Pr₃)₂] (3, C₃₄H₇₄CrP₄Si₂)

A THF solution (5 cm^3) of 179 mg freshly prepared $\text{Li–C}\equiv\text{C–Si-}i\text{-Pr}_3$ (0.95 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ (0.47 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **3** was extracted with *n*-pentane. Crystallization from *n*-pentane produced large brown crystals. Yield: 271 mg (78%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 3.0 (br, 42H, Si^iPr_3), −3.8 (br, 8H, PCH_2), −27.2 (br, 24H, PCH_3) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,900 (w), 2,860 (w) (C–H), 2,360 (m), 1,965 (m) (C \equiv C), 923 (s), 882 (s) (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(triisopropylsilylethynyl)chromium(II), [Cr(dmpe)₂(C \equiv C–SiPh₃)₂] (4, C₅₂H₆₂CrP₄Si₂)

A THF solution (5 cm^3) of 269 mg freshly prepared $\text{Li–C}\equiv\text{C–SiPh}_3$ (0.95 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ (0.47 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **4** was extracted with *n*-pentane. Yield: 315 mg (73%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 8.9 (br, 30H, SiPh_3), −5.9 (br, 8H, PCH_2), −29.3 (br, 24H, PCH_3) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,963 (w), 2,899 (w) (C–H), 1,997 (m), 1,962 (m) (C \equiv C), 1,483 (m), 1,427 (s) (C=C), 924 (s), 886 (s) (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis{(4-trimethylsilyl)-1,3-butadiynide}chromium(II), [Cr(dmpe)₂(C \equiv C–C \equiv C–SiMe₃)₂] (5, C₂₆H₅₀CrP₄Si₂)

A THF solution (5 cm^3) of 122 mg freshly prepared $\text{Li–C}\equiv\text{C–C}\equiv\text{C–SiMe}_3$ (0.95 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ (0.47 mmol). The

temperature was increased to 20 °C and the mixture was stirred for 4 h. The solvent was removed in vacuo and the red solid of **5** was extracted with *n*-pentane. Yield: 241 mg (86%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 2.13 (s, 18H, SiMe_3), −11.4 (br, 8H, PCH_2), −32.1 (br, 24H, PCH_3) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,959 (w), 2,898 (w) (C–H), 2,092 (m), 2,067 (m) ($\text{C}\equiv\text{C}$), 924 (s), 834 (s) (P–C) cm^{-1} ; Raman (633 nm): $\bar{\nu}$ = 2,965, 2,923 (C–H), 2,099, 1,959 ($\text{C}\equiv\text{C}$), 945, 845 (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(phenylethynyl)chromium(II), $[\text{Cr}(\text{dmpe})_2(\text{C}\equiv\text{C}-\text{Ph})_2]$ (**6**, $\text{C}_{28}\text{H}_{42}\text{CrP}_4$)

A THF solution (5 cm^3) of 102 mg freshly prepared $\text{Li}-\text{C}\equiv\text{C}-\text{Ph}$ (0.95 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ (0.47 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **6** was extracted with *n*-pentane. Yield: 235 mg (88%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 33.6 (br, arom. H, 4H), 20.3 (br, arom. H, 4H), −3.1 (br, 8H, PCH_2), −20.2 (br, 40H, PCH_2CH_3), −51.7 (br, arom. H, 2H) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,965 (w), 2,897 (w) (C–H), 2,024 (m) ($\text{C}\equiv\text{C}$), 1,589 (m), 1,480 (s) (C=C), 932 (s), 921 (s) (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis((1-triisopropylsilyl)ethynyl)-4-ethynylbenzene chromium(II), $[\text{Cr}(\text{dmpe})_2(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{Si}^i\text{Pr}_3)_2]$ (**7**, $\text{C}_{50}\text{H}_{82}\text{CrP}_4\text{Si}_2$)

A THF solution (5 cm^3) of 274 mg freshly prepared $\text{Li}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{Si}^i\text{Pr}_3$ (0.95 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ (0.47 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **7** was extracted with *n*-pentane. Yield: 337 mg (78%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 37.0 (br, arom. H, 4H), 1.2 (br, 42H, Si^iPr_3), −10.0 (br, 8H, PCH_2), −33.0 (br, 24H, PCH_3), −53.4 (br, arom. H, 4H) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,942 (w), 2,864 (w) (C–H), 2,155 (m), 1,992 (w) ($\text{C}\equiv\text{C}$), 1,598 (m), 1,494 (s), 1,462 (s) (C=C), 1,017 (s), 995 (s) (P–C), 881 (vs), 831 (vs) (P–F) cm^{-1} ; Raman (514 nm): $\bar{\nu}$ = 2,979, 2,923 (C–H), 2,141, 2,024 ($\text{C}\equiv\text{C}$), 1,594, 1,412 (C=C), 904, 834 (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(tributylstannylethynyl)chromium(II), $[\text{Cr}(\text{dmpe})_2(\text{C}\equiv\text{C}-\text{SnBu}_3)_2]$ (**8**, $\text{C}_{40}\text{H}_{86}\text{CrP}_4\text{Sn}_2$)

A THF solution (5 cm^3) of 305 mg freshly prepared $\text{Li}-\text{C}\equiv\text{C}-\text{SnBu}_3$ (0.95 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ (0.47 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **8** was extracted with *n*-pentane. Yield: 309 mg (67%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 3.28 (s, 54 H,

SnBu_3), −7.3 (br, 8H, PCH_2), −33.8 (br, 24H, PCH_3) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,944 (w), 2,884 (w), 2,821 (w) (C–H), 1,994 (m) ($\text{C}\equiv\text{C}$), 971 (s) (P–C) cm^{-1} ; Raman (633 nm): $\bar{\nu}$ = 2,981, 2,916 (C–H), 1,977 ($\text{C}\equiv\text{C}$) cm^{-1} .

trans-Bis[1,2-bis(diethylphosphino)ethane]bis(trimethylsilylethynyl)chromium(II), $[\text{Cr}(\text{depe})_2(\text{C}\equiv\text{C}-\text{SiMe}_3)_2]$ (**9**, $\text{C}_{30}\text{H}_{66}\text{CrP}_4\text{Si}_2$)

A THF solution (5 cm^3) of 77 mg freshly prepared $\text{Li}-\text{C}\equiv\text{C}-\text{SiMe}_3$ (74 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{depe})_2\text{Cl}_2$ (0.37 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **9** was extracted with *n*-pentane. Crystallization from *n*-pentane produced large yellow–green crystals. Yield: 197 mg (81%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 9.1 (br, 18H, SiMe_3), 5.6 (br, 24H, PCH_3), −5.9 (br, 8H, PCH_2), −17.3 (br, 16H, PCH_2CH_3) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,956 (w), 2,879 (w) (C–H), 1,973 (m) ($\text{C}\equiv\text{C}$), 1,031 (s) (P–C) cm^{-1} .

trans-Bis[1,2-bis(diethylphosphino)ethane]bis(triethylsilylethynyl)chromium(II), $[\text{Cr}(\text{depe})_2(\text{C}\equiv\text{C}-\text{SiEt}_3)_2]$ (**10**, $\text{C}_{36}\text{H}_{78}\text{CrP}_4\text{Si}_2$)

A THF solution (5 cm^3) of 108 mg freshly prepared $\text{Li}-\text{C}\equiv\text{C}-\text{SiEt}_3$ (0.74 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{depe})_2\text{Cl}_2$ (0.37 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **10** was extracted with *n*-pentane. Yield: 198 mg (72%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 5.9 (br, 24H, PCH_2CH_3), 2.4 (br, 30H, SiEt_3), −6.0 (br, 8H, PCH_2), −16.4 (br, 16H, PCH_2CH_3) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,951 (w), 2,872 (w), 2,901 (w) (C–H), 1,965 (m) ($\text{C}\equiv\text{C}$), 1,016 (m), 969 (s) (P–C) cm^{-1} .

trans-Bis[1,2-bis(diethylphosphino)ethane]bis(triisopropylsilylethynyl)chromium(III), $[\text{Cr}(\text{depe})_2(\text{C}\equiv\text{C}-\text{Si}^i\text{Pr}_3)_2]$ (**11**, $\text{C}_{42}\text{H}_{90}\text{CrP}_4\text{Si}_2$)

A THF solution (5 cm^3) of 139 mg freshly prepared $\text{Li}-\text{C}\equiv\text{C}-\text{Si}^i\text{Pr}_3$ (0.74 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{depe})_2\text{Cl}_2$ (0.37 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **11** was extracted with *n*-pentane. Yield: 233 mg (74%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 2.9 (br, 40H, Si^iPr_3), −6.6 (br, 24H, PCH_2CH_3), −19.7 (br, 24H, PCH_2) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,935 (w), 2,859 (w) (C–H), 1,960 (m) ($\text{C}\equiv\text{C}$), 1,031 (s), 994 (s) (P–C) cm^{-1} .

trans-Bis[1,2-bis(diethylphosphino)ethane]bis(triisopropylsilylethynyl)chromium(III), $[\text{Cr}(\text{depe})_2(\text{C}\equiv\text{C}-\text{SiPh}_3)_2]$ (**12**, $\text{C}_{60}\text{H}_{78}\text{CrP}_4\text{Si}_2$)

A THF solution (5 cm^3) of 210 mg freshly prepared $\text{Li}-\text{C}\equiv\text{C}-\text{SiPh}_3$ (0.74 mmol) was added to a THF solution

of 200 mg $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ (0.37 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **12** was extracted with *n*-pentane. Yield: 293 mg (76%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 8.8 (br, 30H, SiPh_3), −6.6 (br, 24H, PCH_2CH_3), −20.0 (br, 24H, PCH_2) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,957 (w), 2,931 (w), 2,874 (w) (C–H), 1,962 (m) ($\text{C}\equiv\text{C}$), 1,483 (w), 1,427 (m) (C=C), 1,028 (s) (P–C) cm^{-1} .

trans-Bis[1,2-bis(diethylphosphino)ethane]bis((4-trimethylsilyl)-1,3-butadiynide)chromium(II), $[\text{Cr}(\text{depe})_2(\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{SiMe}_3)_2]$ (**13**, $\text{C}_{34}\text{H}_{66}\text{CrP}_4\text{Si}_2$)

A THF solution (5 cm^3) of 96 mg freshly prepared $\text{Li}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{SiMe}_3$ (0.74 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{depe})_2\text{Cl}_2$ (0.37 mmol). The temperature was increased to 20 °C and the mixture was stirred for 4 h. The solvent was removed in vacuo and the red solid of **13** was extracted with *n*-pentane. Yield: 219 mg (84%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 4.7 (br, 18H, SiMe_3), −7.0 (br, 16H, PCH_2CH_3), −10.7 (br, 8H, PCH_2), −16.7 (br, 24H, PCH_3) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,957 (s), 2,934 (s) (C–H), 2,098 (s), 2,061 (s) ($\text{C}\equiv\text{C}$), 1,028 (s), 984 (s), 835 (s) (P–C) cm^{-1} ; Raman (514 nm): $\bar{\nu}$ = 2,966, 2,903 (C–H), 2,157, 2,102 ($\text{C}\equiv\text{C}$), 1,070 (P–C) cm^{-1} .

trans-Bis[1,2-bis(diethylphosphino)ethane]bis((phenyl)ethynyl)chromium(II), $[\text{Cr}(\text{depe})_2(\text{C}\equiv\text{C}-\text{Ph})_2]$ (**14**, $\text{C}_{36}\text{H}_{58}\text{CrP}_4$)

A THF solution (5 cm^3) of 101 mg freshly prepared $\text{Li}-\text{C}\equiv\text{C}-\text{Ph}$ (0.74 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{depe})_2\text{Cl}_2$ (0.37 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of **14** was extracted with *n*-pentane. Yield: 217 mg (88%); ^1H NMR (toluene- d_8 , 300 MHz, 22 °C): δ = 32.9 (br, arom. H, 8H), 5.6 (br, 24H, PCH_2CH_3), −6.3 (br, 8H, PCH_2), −17.5 (br, 16H, PCH_2CH_3), −49.7 (br, arom. H, 2H) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,957 (m), 2,893 (m) (C–H), 2,030 (w) ($\text{C}\equiv\text{C}$), 1,589 (m), 1,481 (s) (C=C), 1,028 (s), 905 (s) (P–C) cm^{-1} ; Raman (514 nm): $\bar{\nu}$ = 2,938, 2,902 (C–H), 2,032 ($\text{C}\equiv\text{C}$), 1,592, 1,480 (C=C), 996 (P–C) cm^{-1} .

trans-Bis[1,2-bis(diethylphosphino)ethane]bis((1-triisopropylsilyl)ethynyl)-4-ethynylbenzene)chromium(II), $[\text{Cr}(\text{depe})_2(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{Si}i\text{-Pr}_3)_2]$ (**15**, $\text{C}_{58}\text{H}_{98}\text{CrP}_4\text{Si}_2$)

A THF solution (5 cm^3) of 213 mg freshly prepared $\text{Li}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-\text{Si}i\text{-Pr}_3$ (0.74 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{depe})_2\text{Cl}_2$ (0.37 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the

red solid of **15** was extracted with *n*-pentane. Yield: 281 mg (74%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 36.0 (br, arom. H, 2H), 5.4 (br, PCH_2CH_3 , 24H), 1.2 (br, 42H, $\text{Si}i\text{-Pr}_3$), −5.7 (br, 8H, PCH_2), −17.3 (br, PCH_2CH_3 , 16H), −51.3 (br, arom. H, 2H) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,937 (w), 2,863 (w) (C–H), 2,147 (m), 2,019 (m) ($\text{C}\equiv\text{C}$), 1,591 (s), 1,496 (s) (C=C), 1,028 (s), 994 (s) (P–C) cm^{-1} .

trans-Bis[1,2-bis(diethylphosphino)ethane]bis(tributylstannylethynyl)chromium(II), $[\text{Cr}(\text{depe})_2(\text{C}\equiv\text{C}-\text{SnBu}_3)_2]$ (**16**, $\text{C}_{48}\text{H}_{102}\text{CrP}_4\text{Sn}_2$)

A THF solution (5 cm^3) of 237 mg freshly prepared $\text{Li}-\text{C}\equiv\text{C}-\text{SnBu}_3$ (0.74 mmol) was added to a THF solution of 200 mg $\text{Cr}(\text{depe})_2\text{Cl}_2$ (0.37 mmol). The temperature was increased to 20 °C and the mixture was stirred for 10 h. The solvent was removed in vacuo and the red solid of $\text{Cr}(\text{depe})_2(\text{C}\equiv\text{C}-\text{SnBu}_3)_2$ was extracted with *n*-pentane. Yield: 319 mg (79%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): δ = 5.7 (br, 54H, SnBu_3), −3.8 (br, 24H, PCH_2CH_3), −19.2 (br, 24H, PCH_2) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,957 (w), 2,926 (w), 2,873 (w) (C–H), 2,020 (m) ($\text{C}\equiv\text{C}$), 1,028 (m), 960 (s) (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(trimethylsilylethynyl)chromium(III) hexafluorophosphate, $[\text{Cr}(\text{dmpe})_2(\text{C}\equiv\text{C}-\text{SiMe}_3)_2][\text{PF}_6]$ (**17**, $\text{C}_{22}\text{H}_{50}\text{CrF}_6\text{P}_5\text{Si}_2$)

A CH_2Cl_2 solution of 200 mg **1** (0.37 mmol) was added to a CH_2Cl_2 suspension of 121 mg $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ (0.37 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et_2O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH_2Cl_2 was evaporated to give the title compound. Crystallization from a mixture of dichloromethane and ether at −35 °C produced single orange crystals. Yield: 235 mg (92%); ^1H NMR (CD_2Cl_2 , 300 MHz, 22 °C): δ = 10.1 (br, 32H, dmpe), 0.15 (s, 18 H, $\text{Si}(\text{CH}_3)_3$) ppm; ^{31}P { ^1H } NMR (CD_2Cl_2 , 121.5 MHz, 22 °C): δ = −145.6 (sept, $^1J_{\text{PF}} = 719$ Hz, PF_6^-) ppm; ^{19}F { ^1H } NMR (CD_2Cl_2 , 282.3 MHz, 22 °C): δ = −74.2 (d, $^1J_{\text{FP}} = 719$ Hz, PF_6^-) ppm; IR (CH_2Cl_2 , 22 °C): $\bar{\nu}$ = 2,993 (w), 2,902 (w) (C–H), 2,237 (m), 2,081 (m) ($\text{C}\equiv\text{C}$), 952 (s), 933 (s) (P–C), 849 (vs) (P–F) cm^{-1} ; Raman (514 nm): $\bar{\nu}$ = 2,978, 2,910 (C–H), 2,000 ($\text{C}\equiv\text{C}$), 693, 651 (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(triethylsilylethynyl)chromium(III) hexafluorophosphate, $[\text{Cr}(\text{dmpe})_2(\text{C}\equiv\text{C}-\text{SiEt}_3)_2][\text{PF}_6]$ (**18**, $\text{C}_{28}\text{H}_{62}\text{CrF}_6\text{P}_5\text{Si}_2$)

A CH_2Cl_2 solution of 200 mg **2** (0.32 mmol) was added to a CH_2Cl_2 suspension of 105 mg $[\text{Cp}_2\text{Fe}][\text{PF}_6]$

(0.32 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 228 mg (92%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = 12.9 (br, 32H), 0.96 (s, 30 H, Si(CH₂CH₃)₃) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −145.6 (sept, ¹J_{P-F} = 717 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −75.2 (d, ¹J_{F-P} = 717 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,946 (w), 2,910 (w), 2,874 (w) (C–H), 2,066 (m) (C≡C), 949 (s), 931 (s) (P–C), 831 (vs) (P–F) cm^{−1}.

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis (triisopropylsilyl)ethynylchromium(III) hexafluorophosphate, [Cr(dmpe)₂(C≡C–Si–Pr₃)₂][PF₆] (**19**, C₃₄H₇₄CrF₆P₅Si₂)

A CH₂Cl₂ solution of 200 mg **3** (0.27 mmol) was added to a CH₂Cl₂ suspension of 90 mg [Cp₂Fe][PF₆] (0.27 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 217 mg (91%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = 4.1 (br, 32H, dmpe), 1.19 (s, 42 H, Si–Pr₃) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −144.6 (sept, ¹J_{PF} = 713 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −73.9 (d, ¹J_{FP} = 713 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,945 (w), 2,865 (w) (C–H), 1,984 (m) (C≡C), 951 (s), 931 (s) (P–C), 828 (vs) (P–F) cm^{−1}.

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis (triphenylsilyl)ethynylchromium(III) hexafluorophosphate, [Cr(dmpe)₂(C≡C–SiPh₃)₂][PF₆] (**20**, C₅₂H₆₂CrF₆P₅Si₂)

A CH₂Cl₂ solution of 200 mg **4** (0.22 mmol) was added to a CH₂Cl₂ suspension of 72 mg [Cp₂Fe][PF₆] (0.22 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 190 mg (81%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = 9.5 (br, 32H, dmpe), 7.78 (s, 30H, SiPh₃) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −146.5 (sept, ¹J_{PF} = 715 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −74.6 (d, ¹J_{FP} = 715 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 3,071 (w), 2,918 (w) (C–H), 2,001 (m) (C≡C), 1,587 (m), 1,491 (s) (C=C), 975 (s) (P–C), 832 (vs) (P–F) cm^{−1}.

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis ((4-trimethylsilyl)-1,3-butadiynide)chromium(III) hexafluorophosphate, [Cr(dmpe)₂(C≡C–C≡C–SiMe₃)₂][PF₆] (**21**, C₂₆H₅₀CrF₆P₅Si₂)

A CH₂Cl₂ solution of 200 mg **5** (0.34 mmol) was added to a CH₂Cl₂ suspension of [Cp₂Fe][PF₆] (111 mg, 0.34 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 211 mg (84%); ¹H NMR (C₆D₆, 300 MHz, 22 °C): δ = 1.62 (s, 18 H, SiMe₃), −17.2 (br, 8H, PCH₂), −61.6 (br, 24H, PCH₃) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −145.6 (sept, ¹J_{PF} = 713 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −74.5 (d, ¹J_{FP} = 713 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,963 (w), 2,910 (w) (C–H), 2,115 (m), 1,983 (m) (C≡C), 950 (s), 931 (s) (P–C), 827 (vs) (P–F) cm^{−1}; Raman (633 nm): $\bar{\nu}$ = 2,981, 2,933 (C–H), 2,148, 2,111, 1,985 (C≡C), 959, 853 (P–C) cm^{−1}.

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis ((phenyl)ethynyl)chromium(III) hexafluorophosphate, [Cr(dmpe)₂(C≡C–Ph)₂][PF₆] (**22**, C₂₈H₄₂CrF₆P₅)

A CH₂Cl₂ solution of 200 mg **6** (0.35 mmol) was added to a CH₂Cl₂ suspension of 117 mg [Cp₂Fe][PF₆] (0.35 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Crystallization from a mixture of dichloromethane and ether at −35 °C produced single orange–yellow crystals. Yield: 224 mg (90%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = 39.5 (br, 8H, PCH₂), −19.6 (br, 40H, PCH₂CH₃) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −145.3 (sept, ¹J_{PF} = 714 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −74.6 (d, ¹J_{FP} = 714 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,909 (w) (C–H), 2,164 (m) (C≡C), 1,484 (s), 1,413 (s) (C=C), 952 (s), 931 (s) (P–C), 829 (vs) (P–F) cm^{−1}.

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis ((1-triisopropylsilyl)ethynyl)-4-ethynylbenzene) chromium(III) hexafluorophosphate, [Cr(dmpe)₂(C≡C–C₆H₄–C≡C–Si–Pr₃)₂][PF₆] (**23**, C₅₀H₈₂CrF₆P₅Si₂)

A CH₂Cl₂ solution of 200 mg **7** (0.22 mmol) was added to a CH₂Cl₂ suspension of 72 mg [Cp₂Fe][PF₆] (0.22 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was

washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 210 mg (91%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = 43.1 (br, 24H, PCH₃), 1.3 (br, 42H, Si¹Pr₃), −58.4 (br, 8H, PCH₂) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −144.8 (sept, ¹J_{PF} = 715 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −0.2 (d, ¹J_{FP} = 715 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,945 (w), 2,866 (w) (C–H), 2,155 (m), 1,998 (w) (C≡C), 1,597 (m), 1,493 (s), 1,467 (s) (C=C), 949, 931 (s) (P–C), 831 (vs) (P–F) cm^{−1}; Raman (514 nm): $\bar{\nu}$ = 2,986, 2,927 (C–H), 2,213, 2,157 (C≡C), 1,603, 1,583 (C=C) cm^{−1}.

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis(tributylstannylolethynyl)chromium(III) hexafluorophosphate, [Cr(dmpe)₂(C≡C–SnBu₃)₂][PF₆] (24, C₄₀H₈₆CrF₆P₅Sn₂)

A CH₂Cl₂ solution of 200 mg **8** (0.20 mmol) was added to a CH₂Cl₂ suspension of 68 mg [Cp₂Fe][PF₆] (0.20 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 173 mg (77%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = −5.3 (br, dmpe, 32H) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −146.3 (sept, ¹J_{PF} = 714 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −75.3 (d, ¹J_{FP} = 714 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,963 (w), 2,899 (w) (C–H), 1,997 (m), 1,961 (m) (C≡C), 922, (P–C), 885 (s) (P–F) cm^{−1}; Raman (514 nm): $\bar{\nu}$ = 2,987, 2,915 (C–H), 1,973, 1,928 (C≡C), 949 (P–C) cm^{−1}.

trans-Bis[1,2-bis(diethylphosphino)ethane]bis(trimethylsilylolethynyl)chromium(III) hexafluorophosphate, [Cr(depe)₂(C≡C–SiMe₃)₂][PF₆] (25, C₃₀H₆₆CrF₆P₅Si₂)

A CH₂Cl₂ solution of 200 mg **9** (0.30 mmol) was added to a CH₂Cl₂ suspension of 99 mg [Cp₂Fe][PF₆] (0.30 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Crystallization from a mixture of dichloromethane and ether at −35 °C produced single orange crystals. Yield: 217 mg (90%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = 10.2 (br, 24H, PCH₂), 4.2 (br, 24H, PCH₂PCH₃), 1.26 (s, 18 H, SiMe₃) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −144.8 (sept, ¹J_{PF} = 716 Hz, PF₆[−]) ppm; ¹⁹F {¹H}

NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −74.8 (d, ¹J_{FP} = 716 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,958 (w), 2,890 (w) (C–H), 2,005 (m) (C≡C), 1,043 (s) (P–C), 828 (vs) (P–F) cm^{−1}.

trans-Bis[1,2-bis(diethylphosphino)ethane]bis(triethylsilylolethynyl)chromium(III) hexafluorophosphate, [Cr(depe)₂(C≡C–SiEt₃)₂][PF₆] (26, C₃₆H₇₈CrF₆P₅Si₂)
A CH₂Cl₂ solution of 200 mg **10** (0.27 mmol) was added to a CH₂Cl₂ suspension of 89 mg [Cp₂Fe][PF₆] (0.27 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Crystallization from a mixture of dichloromethane and ether at −35 °C produced single yellow crystals. Yield: 208 mg (87%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = 10.1 (br, 24H, PCH₂), 4.2 (br, 24H, PCH₃), 1.23 (s, 18 H, SiEt₃) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −144.3 (sept, ¹J_{PF} = 718 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −74.4 (d, ¹J_{FP} = 718 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,947 (w), 2,875 (w) (C–H), 1,996 (m) (C≡C), 1,018 (s), 972 (s) (P–C), 834 (vs) (P–F) cm^{−1}.

trans-Bis[1,2-bis(diethylphosphino)ethane]bis(triisopropylsilylolethynyl)chromium(III) hexafluorophosphate, [Cr(depe)₂(C≡C–Siⁱ–Pr₃)₂][PF₆] (27, C₄₂H₉₀CrF₆P₅Si₂)

A CH₂Cl₂ solution of 200 mg **11** (0.23 mmol) was added to a CH₂Cl₂ suspension of 78 mg [Cp₂Fe][PF₆] (0.23 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 208 mg (91%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = 1.1 (br, Siⁱ–Pr₃), −30.2 (br, depe) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −145.7 (sept, ¹J_{PF} = 713 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −74.1 (d, ¹J_{FP} = 713 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,941 (w), 2,862 (w) (C–H), 1,983 (m) (C≡C), 1,586 (m), 1,464 (m), 1,413 (s) (C=C), 1,042 (s), 987 (s) (P–C), 833 (vs) (P–F) cm^{−1}.

trans-Bis[1,2-bis(diethylphosphino)ethane]bis(triphenylsilylolethynyl)chromium(III) hexafluorophosphate, [Cr(depe)₂(C≡C–SiPh₃)₂][PF₆] (28, C₆₀H₈₈CrF₆P₅)

A CH₂Cl₂ solution of 200 mg **12** (0.19 mmol) was added to a CH₂Cl₂ suspension of 64 mg [Cp₂Fe][PF₆] (0.19 mmol). This mixture was stirred for 1 h at room

temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 211 mg (94%); ¹H NMR (C₆D₆, 300 MHz, 22 °C): δ = 9.3 (br, 40H, SiPh₃), −17.9 (br, 24H, PCH₂CH₃), −33.6 (br, 24H, PCH₂) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −144.6 (sept, ¹J_{PF} = 714 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −74.8 (d, ¹J_{FP} = 714 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,970 (w), 2,939 (w) (C–H), 1,996 (m) (C≡C), 1,493 (m), 1,458 (s) (C=C), 1,028 (s) (P–C), 834 (vs) (P–F) cm^{−1}.

trans-Bis[1,2-bis(diethylphosphino)ethane]bis
{(4-trimethylsilyl)-1,3-butadiynide}chromium(II)
hexafluorophosphate, [Cr(depe)₂(C≡C–C≡C–SiMe₃)₂]
[PF₆] (29, C₃₄H₆₆CrF₆P₅Si₂)

A CH₂Cl₂ solution of 200 mg **13** (0.28 mmol) was added to a CH₂Cl₂ suspension of 94 mg [Cp₂Fe][PF₆] (0.28 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 217 mg (91%); ¹H NMR (C₆D₆, 300 MHz, 22 °C): δ = 9.8 (br, 8H, PCH₂), 1.18 (s, 18H, SiMe₃), −4.7 (br, 16H, PCH₂CH₃), −16.8 (br, 24H, PCH₃) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −145.5 (sept, ¹J_{PF} = 714 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −74.6 (d, ¹J_{FP} = 714 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,966 (w), 2,885 (w) (C–H), 2,349 (m), 2,305 (m) (C≡C), 1,030 (m) (P–C), 826 (s) (P–F) cm^{−1}.

trans-Bis[1,2-bis(diethylphosphino)ethane]bis
((phenyl)ethynyl)chromium(III) hexafluorophosphate,
[Cr(depe)₂(C≡C–Ph)₂][PF₆] (30, C₃₆H₅₈CrF₆P₅)

A CH₂Cl₂ solution of 200 mg **14** (0.30 mmol) was added to a CH₂Cl₂ suspension of 99 mg [Cp₂Fe][PF₆] (0.30 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 209 mg (86%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = 40.9 (br, 8H, PCH₂), −17.9 (br, 40H, PCH₂CH₃) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −145.3 (sept, ¹J_{PF} = 715 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −74.6 (d, ¹J_{FP} = 715 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,938 (s), 2,881 (s) (C–H), 1,987 (s) (C≡C),

1,593 (m), 1,484 (s) (C=C), 1,027 (s) (P–C), 832 (vs) (P–F) cm^{−1}.

trans-Bis[1,2-bis(diethylphosphino)ethane]bis
{(1-triisopropylsilyl)ethynyl}-4-ethynylbenzene
chromium(II) hexafluorophosphate, [Cr(depe)₂
(C≡C–C₆H₄–C≡C–Si–Pr₃)₂][PF₆]
(31, C₅₈H₉₈CrF₆P₅)

A CH₂Cl₂ solution of 200 mg **15** (0.19 mmol) was added to a CH₂Cl₂ suspension of 64 mg [Cp₂Fe][PF₆] (0.19 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 207 mg (93%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = 17.3 (br, 24H, PCH₂), 1.12 (br, 42H, Si–Pr₃), −15.7 (br, 24H, PCH₂CH₃) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −145.9 (sept, ¹J_{PF} = 716 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −73.6 (d, ¹J_{FP} = 716 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,940 (w), 2,864 (w) (C–H), 2,149 (m), 2,081 (m) (C≡C), 1,593 (m), 1,493 (s), 1,458 (s) (C=C), 1,029 (s) (P–C), 831 (vs) (P–F) cm^{−1}.

trans-Bis[1,2-bis(diethylphosphino)ethane]bis
(tributylstannylethynyl)chromium(III)
hexafluorophosphate, [Cr(depe)₂(C≡C–SnBu₃)₂]
[PF₆] (32, C₄₈H₁₀₂CrF₆P₅Sn₂)

A CH₂Cl₂ solution of 200 mg **16** (0.18 mmol) was added to a CH₂Cl₂ suspension of 61 mg [Cp₂Fe][PF₆] (0.18 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et₂O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH₂Cl₂ was evaporated to give the title compound. Yield: 187 mg (84%); ¹H NMR (CD₂Cl₂, 300 MHz, 22 °C): δ = 2.1 (br, SnBu₃), −4.7 (br, depe) ppm; ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 22 °C): δ = −145.4 (sept, ¹J_{PF} = 715 Hz, PF₆[−]) ppm; ¹⁹F {¹H} NMR (CD₂Cl₂, 282.3 MHz, 22 °C): δ = −74.8 (d, ¹J_{FP} = 715 Hz, PF₆[−]) ppm; IR (ATR, 22 °C): $\bar{\nu}$ = 2,947 (w), 2,898 (w) (C–H), 2,014 (m) (C≡C), 1,064 (m), 969 (s) (P–C), 865 (vs) (P–F) cm^{−1}.

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis
(ethynyl)chromium(II), [Cr(dmpe)₂(C≡C–H)₂]
(33, C₁₆H₃₄CrP₄)

A THF solution (5 cm³) of 45.4 mg Na–C≡C–H (0.95 mmol) was added dropwise, very slowly, to a solution of 200 mg Cr(dmpe)₂Cl₂ (0.47 mmol) in 20 cm³ THF. The mixture was stirred for 10 h. The solvent was removed in vacuo and the dark brown solid was extracted

with *n*-pentane. Yield: 141 mg (74%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): $\delta = -13.2$ (br, 8H, PCH_2), -33.8 (br, 24H, PCH_3) ppm; IR (THF, 22 °C): $\bar{\nu} = 3,270$ (m) ($-\text{C}\equiv\text{C}-\text{H}$), 2,952 (w), 2,983 (w) (C–H), 1,919 (s) ($\text{C}\equiv\text{C}$), 986 (s) (P–C) cm^{-1} ; Raman (633 nm): $\bar{\nu} = 2,968$, 2,903 (C–H), 1,897 ($\text{C}\equiv\text{C}$), 944 (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]bis

(ethynyl)chromium(III) hexafluorophosphate,

$[\text{Cr}(\text{dmpe})_2(\text{C}\equiv\text{C}-\text{H})_2][\text{PF}_6]$ (**34**, $\text{C}_{16}\text{H}_{34}\text{CrF}_6\text{P}_5$)

A CH_2Cl_2 solution of 200 mg **33** (0.50 mmol) was added to a CH_2Cl_2 suspension of 165 mg $[\text{Cp}_2\text{Fe}][\text{PF}_6]$ (0.50 mmol). This mixture was stirred for 1 h at room temperature. The solvent was evaporated to give a brown solid, which was washed with Et_2O until the solvent became colourless. The solid was dissolved in dichloromethane and the solution was filtered through Celite. The CH_2Cl_2 was evaporated to give the title compound. Yield: 230 mg (84%); ^1H NMR (CD_2Cl_2 , 300 MHz, 22 °C): $\delta = 24.8$ (br, 32H, dmpe) ppm; ^{31}P $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 121.5 MHz, 22 °C): $\delta = -147.4$ (sept, $^1J_{\text{PF}} = 714$ Hz, PF_6^-) ppm; ^{19}F $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 282.3 MHz, 22 °C): $\delta = -75.2$ (d, $^1J_{\text{FP}} = 714$ Hz, PF_6^-) ppm; IR (ATR, 22 °C): $\bar{\nu} = 3,270$ (m) ($-\text{C}\equiv\text{C}-\text{H}$), 2,977 (w), 2,911 (w) (C–H), 1,935 (m) ($\text{C}\equiv\text{C}$), 951 (s) (P–C), 747 (vs) (P–F) cm^{-1} ; Raman (633 nm): 2,985, 2,918 (C–H), 1,929 ($\text{C}\equiv\text{C}$) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]chloro

(ethynyl)chromium(II), $[\text{CrCl}(\text{dmpe})_2(\text{C}\equiv\text{C}-\text{H})]$

(**35**, $\text{C}_{14}\text{H}_{33}\text{ClCrP}_4$)

A THF solution (5 cm^3) of 22.6 mg $\text{Na}-\text{C}\equiv\text{C}-\text{H}$ (0.47 mmol) was added dropwise, very slowly, to a THF solution of 200 mg $\text{Cr}(\text{dmpe})_2\text{Cl}_2$ (0.47 mmol). The mixture was stirred for 10 h. The solvent was removed in vacuo and the dark brown solid was washed with *n*-pentane and the corresponding compound was extracted with toluene. Crystallization from toluene produced large red-orange crystals. Yield: 120 mg (62%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): $\delta = -13.2$ (br, 8H, PCH_2), -33.9 (br, 24H, PCH_3) ppm; IR (ATR, 22 °C): $\bar{\nu} = 3,248$ (m) ($-\text{C}\equiv\text{C}-\text{H}$), 3,010 (w), 2,860 (w) (C–H), 2,030 (m) ($\text{C}\equiv\text{C}$), 971 (s), 899 (s) (P–C) cm^{-1} .

trans-Bis[1,2-bis(dimethylphosphino)ethane]chloro

(trimethylsilyl)ethynyl)chromium(II), $[\text{CrCl}(\text{dmpe})_2$

($\text{C}\equiv\text{C}-\text{SiMe}_3$)] (**37**, $\text{C}_{11}\text{H}_{41}\text{CrP}_4\text{Si}$)

A THF solution of 200 mg **35** (0.48 mmol) was cooled at -80 °C and 1 equiv. *n*-BuLi 1.6 M in hexane (0.48 cm^3) was added with constant stirring. After stirring for 2 h, 1 equiv. Me_3SiCl (52 mg, 0.48 mmol) was added at -80 °C. The temperature of the mixture was increased to 20 °C and

the mixture was stirred for 10 h. The solvent was removed in vacuo and the corresponding compound was extracted with toluene. Yield: 165 mg (77%); ^1H NMR (C_6D_6 , 300 MHz, 22 °C): $\delta = 9.1$ (s, 18 H, $\text{Si}(\text{CH}_3)_3$), -13.2 (br, 8H, PCH_2), -34.0 (br, 24H, PCH_3) ppm; IR (ATR, 22 °C): $\bar{\nu} = 2,943$ (w), 2,919 (w) (C–H), 1,888 (m) ($\text{C}\equiv\text{C}$), 896 (s), 840 (s) (P–C) cm^{-1} .

Crystal structure determination

Suitable crystals of **1**, **6**, and **35** were mounted on the tip of a glass fibre using polybutene oil as protecting agent. The crystals were cooled to 183(2) K by use of an Oxford cryogenic system. Determination of the unit cell parameters and collection of the intensity of reflections were performed with an image plate detector system (Stoe IPDS one-circle diffractometer) with graphite monochromated Mo K_α radiation ($\lambda = 0.71073$ Å) by using Stoe IPDS software [41, 42]. Totals of 23,433, 45,910, and 22,015 reflections were collected for **1**, **6**, and **35** and resulted in 5,440 ($R_{\text{int}} = 0.046$), 20,597 ($R_{\text{int}} = 0.0571$), and 3,893 ($R_{\text{int}} = 0.1189$) unique reflections. The structures were solved with direct methods and refined using the software SHELXS97 and SHELXL97 [43]. Lorentz and polarisation corrections were done with INTEGRATE, and numerical absorption corrections (21, 20, and eight crystal faces were measured with FACE-it-Video) were performed with XRED in the IPDS software. Compound **6** was initially solved in the triclinic space group C-1 with four independent molecules in the asymmetric unit. A check for higher symmetry with PLATON [44] resulted in the orthorhombic space group *Pccn*, where the triclinic unit cell with $a = 19.3117(14)$ Å, $b = 19.3177(14)$ Å, $c = 20.3244(15)$ Å, $\alpha = 90.029(9)^\circ$, $\beta = 89.992(9)^\circ$, $\gamma = 93.767(9)^\circ$ and the respective intensity reflections had to be transformed by the matrix $(-1/2, -1/2, 0; 0, 0, -1; 1/2, -1/2, 0)$. Selected crystallographic data are given in Table 1, whereas more details of the crystal structures are available in the respective CIF files. A common feature in the presented structures (Figs. 1, 2, 5) is that half the molecules are completed by a crystallographic inversion centre, where the Cr atoms reside on their special positions.

Crystallographic data (excluding structure factors) for the structures given in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 698031, 622090, 698032. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1 Selected crystallographic data of **17**, **22**, and **35**

Compound	17	22	35
Empirical formula	C ₂₂ H ₅₀ F ₆ P ₅ Si ₂	C ₂₉ H ₄₄ Cl ₂ CrF ₆ P ₅	C ₂₁ H ₄₁ ClCrP ₄
Formula weight	691.65	784.39	504.87
Crystal habit, colour	Block, yellow	Block, orange–yellow	Plate, red–orange
Crystal dimensions/mm ³	0.33 × 0.27 × 0.22	0.31 × 0.29 × 0.29	0.21 × 0.15 × 0.05
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>C2/c</i>	<i>Pccn</i>	<i>P2₁/c</i>
<i>a</i> /Å	19.2357(11)	13.2013(10)	8.6134(14)
<i>b</i> /Å	12.5515(9)	20.3239(16)	11.3010(14)
<i>c</i> /Å	15.8493(10)	14.0992(9)	14.1020(19)
α /deg	90	90	90
β /deg	108.694(7)	90	101.652(18)
γ /deg	90	90	90
<i>V</i> /Å ³	3,624.7(4)	3,782.8(5)	1,344.4(3)
<i>Z</i>	4	4	2
<i>T</i> /K	183(2)	183(2)	183(2)
<i>D</i> _{calcd} /gcm ^{−3}	1.267	1.377	1.247
μ /mm ^{−1}	0.645	0.704	0.768
<i>R</i> ^a , <i>wR</i> ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0385, 0.905	0.0461, 0.1177	0.0351, 0.0630
<i>R</i> ^a , <i>wR</i> ^b (all data)	0.0622, 0.0955	0.0820, 0.1288	0.1172, 0.0758

$$^a R(F) = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$$

$$^b Rw(F^2) = [\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]^{1/2}$$

Acknowledgments Funding from the Swiss National Science Foundation (SNSF) and from the University of Zürich is gratefully acknowledged.

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